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Comment on ''Computational studies on organic reactivity in ionic liquids'' by C. Chiappe and C. S. Pomelli, *Phys. Chem. Chem. Phys.*, 2013, 15, 412

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In their perspective ''Computational studies on organic reactivity in ionic liquids'' Chiappe and Pomelli[1] have written a short paragraph excluding COSMO-RS as a potential method for estimating reaction thermodynamics in ionic liquids. They write:

''COSMO-RS, a model based on a simplified version of the polarizable continuum model, which is strongly parameterized, has been used to estimate the thermodynamics of a solvent. However, this model is unable to give a precise physical description of the system and the parameterization set does not include reaction barriers; therefore, COSMO-RS is not suitable for reactivity studies.''

Since the authors reference just one out of many application papers by COSMO-RS users[2] and do not give conclusive reasoning for their statement, we feel the necessity to comment on the usability of COSMO-RS for estimating reaction thermodynamics and kinetics in ionic liquid media.

As a matter of fact, COSMO-RS[3,4] is based on the Conductor-like Screening Model (COSMO),[5] and COSMO is – although developed independently – a simpler and thus numerically more efficient continuum solvation model than the polarizable continuum model. Nevertheless it must be pointed out that there is no proof in the literature that the conceptual simplifications of COSMO have any negative influence on the quality of results. Instead, it turned out to be more accurate with respect to the outlying charge problem, and for that reason the COSMO boundary condition has even been integrated into the polarizable continuum model as C-PCM.[6]

COSMO-RS is a combination of COSMO – used in its limit of the perfect conductor – and a statistical thermodynamics of pair-wise interacting surface segments, where the surface interactions are quantified based on the COSMO polarization charge densities. By that COSMO-RS treats solutes and solvents on the same quantum chemical footing, and introduces the concepts of mixtures and temperature dependence in a natural, thermodynamically consistent way. As a result it does not require any chemistry dependent parameters for the solvents, which in almost all other solvation models require special parameterization. Altogether COSMO-RS thus has less adjustable parameters than most other solvation models. If the authors want to claim the opposite, they shall clearly demonstrate this claim. Quite surely COSMO-RS overall has by far less adjustable parameters than the specially adapted IL-force fields required for the QM/MM, recommended as the method of choice in this perspective.

COSMO-RS has been proven in a large number of application papers to be well applicable to study solvation thermodynamics in ionic liquids, even though initially completely parameterized on neutral compounds and solvents. A Google-Scholar search for ''Ionic Liquids'' in combination with ''COSMO-RS'' yields 874 hits as of Nov. 29, 2012. On the other hand, COSMO-RS has been proven to be applicable to study reaction thermodynamics and reaction kinetics in solution.[7–9] Very recently, various authors have reported the application of COSMO-RS to the study of chemical absorption of CO_2 in ionic liquids.[10,11] The trends predicted for the thermodynamic properties of different ILs using COSMO-RS, such as CO_2 solubility, reaction enthalpy, and solvent reversal temperature, were verified by experimental data.[10,11] These results suggest that COSMO-RS can be successfully used to predict reaction thermodynamics in systems involving ILs, providing a useful computational tool for the development of new CO_2 absorbents. To our knowledge, COSMO-RS applications to estimate reaction

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kinetics in IL-based systems have not been reported, however, we do not see any reason why COSMO-RS should not be applicable to study reaction kinetics in ionic liquids, as it has been done with other solvation methods to evaluate the solvent influence. Of course, in the case of chemical reactions where the role of the IL is not only that of a medium but also of a catalyst, an appropriate choice of the explicitly considered species is required, which means that any really chemically interfering ion of the IL has to be included in the description. This comprises cations and anions acting as Brønsted acids and bases, respectively, with substantial proton transfer in the transition state or intermediates, but also *e.g.* nucleophilic or Lewis acid catalysis by constituents of the IL or species released from it. These species should however also be included in the QM part of a QM/MM description of the system. Also in these cases, COSMO-RS treatment of the remaining effects from not chemically interacting solvent ions is expected to yield an even more accurate access to activation barriers and thus kinetics.

In summary we consider the statements made about COSMO-RS in this perspective as not at all based on an objective analysis or on own experience.

Hereby, one of the authors, Andreas Klamt, declares a potential conflict of interest, since he is commercially distributing one of the implementations of the COSMO-RS method out of his company COSMOlogic GmbH&CoKG.

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